AT THE ENTERPRISES AND INSTITUTES

PREDICTION OF THE STRUCTURE OF SINTERED BIOACTIVE COMPOSITE MATERIALS FOR DENTAL IMPLANTS

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Results of experimental studies of optimizing the process of sintering in bioactive composite materials based on a silicate matrix and hydroapatite are described. To estimate and predict the technological, mechanical, and biological properties of materials, a sinterability index is proposed, which is the ratio between the specific surface areas of the matrix and the filler. A functional correlation between the sinterability index and the content and granulometric composition of the filler is identified. Sintered composites can be used for intrabone dental implants.

Combining achievements in chemistry, medicine, and medical engineering has brought about a new direction in the science of materials, namely, development of biocompatible glasses, ceramics, polymers, metal alloys and composites, which are used to make prostheses capable of replacing not only bone and joints but also roots and crowns of teeth. A tooth has a heterogeneous composition and structure; it consists mainly of hard tissues, such as dentine, enamel, and cement.

Aesthetics has an important role in dental prosthetics. Development of artificial teeth is of intense current interest. Great attention is paid to this subject by physicians and researchers of materials. Modifying materials for dental implants primarily concerns their chemical resistance, strength, and extending their service life.

The best known developments in this sphere imply production of artificial teeth of different designs using various materials classified as biologically inert, which do not stimulate natural osteogenesis. Doctors in this case mainly use mechanical methods for fixing an implant in the alveolar crest. Contemporary stomatology uses laminar, pin, and spiral dental implants. Among the most common materials for intrabone implants are titanium and titanium-based alloys: VT1-00 and VT1-0, known as technically pure titanium.

Tooth crowns fixed on such intrabone implant in their exterior appearance do not differ from "natural" crowns. However, a metallic implant is an alien body in the human organism, which leads to destruction of surrounding bone tissues limiting the implant service life to 10 – 15 years.

In view of the above it has become necessary to develop artificial implant materials combining high physicochemical and mechanical parameters with biological compatibility with live tissue. Such materials include bioceramics, bioglasses, bioceram, and biocomposites of various compositions.

The main principle used as the basis for producing bioactive materials consists in artificial reproduction of the chemical and phase composition of the mineral components of bone.

It is known that tooth enamel and dentine consist of different types of apatite; however, the main one is hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$. The atomic ratio Ca : P in bone HA may vary from 1.50 to 1.67, which corresponds to a series of calcium phosphates from tricalcium phosphate (TCP) to HA. Thus, tooth enamel has the following composition of inorganic material (here and elsewhere wt.%): 75.04 HA, 12.06 carbonate-apatite, 4.39 chlorapatite, 0.663 fluorapatite, 1.33 $CaCO_3$, and 1.62 $MgCO_3$. The introduction of bioactive inorganic materials into clinical practice expands the possibilities of up-to-date dental prosthetics, helps to develop new methods for tooth treatment, and extends the service life of implants in a human body.

The heterogeneous structure of the tooth is well reproduced in wholly ceramic crowns which simulate the natural structure of the tooth. In this case preference is given to selecting layers with different degrees of transparency [1].

The purpose of this study is to optimize compositions of porous permeable composite materials, whose mechanical strength and volume mass could correspond to different sites of natural teeth. For this purpose in designing a series of ma-

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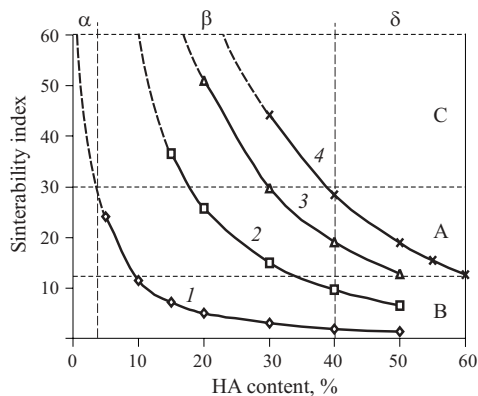[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

Fig. 1. Sinterability index of material versus content of HA with particle size of 20 (*1*), 100 (*2*), 200 (*3*), and 300 μm (*4*).

terials with preset ceramic, mechanical, and biological properties, the granulometric composition of filler (HA) varies from 10 to 300 μm and its content varies from 10 to 50%. The hydrophilic matrix is made of glass of the composition (%): 73.0 SiO_2, 3.5 Al_2O_3, 1.0 MgO, 7.0 CaO, 2.5 B_2O_3, and 13.0 R_2O. Implanting these materials ensures their lifelong service.

The biological properties of calcium-phosphate biocomposite materials depend on their content of calcium phosphates, such as HA and β-TCP. At the same time it is known that phosphate content in a material depends on its granulometric composition. Thus, an increased content of HA (45% and more) in a known material named BAK-1000 is achieved due to introducing grains of size 200 – 900 μm into the initial mixture. The use of finer fractions of size up to 50 μm allows for introducing not more than 10 – 15% HA. The mechanical strength in this case grows 2 – 3 times, however, the biological properties deteriorate [2].

Figure 1 arbitrarily shows three zones of biological activity of calcium-phosphate materials: α) bioinert, β) biocompatible, and δ) bioactive with HA content over 40%.

The bioactive filler in our case was synthesized HA with the atomic ratio Ca : P = 1.67 produced by the wet method in the reaction of precipitation of $Ca(OH)_2$ with H_3PO_4. The resulting finely dispersed HA powder has particles sized 10 – 30 μm [2, 3]. This powder has a very high specific surface area, which prevents introducing it in an amount of more than 10% of the composite material and still obtain a strong and well sintered sample at a temperature not higher than 850°C. A higher sintering temperature impairs the resorption capacity of HA in physiological media.

A sintering schedule was determined based on the characteristic temperatures of the silicate matrix, provided that the maximum temperature would correspond to dynamic viscosity $10^{7.5}$ Pa · sec. The ratio of the specific surface areas of the amorphous silicate matrix and the filler has a great significance in sintering samples. To estimate the pro-

cess of powder sintering, their specific surface areas were calculated [4]:

$$S = \frac{6}{\rho} \sum_{i=1}^{i=n} \frac{\rho_i}{d_i},$$

where S is the total surface area of the material; ρ is the density of the material; ρ_i is he volume mass of material of the particular fraction; d_i is the mean grain diameter, $d_i = \frac{1}{2}(d_{1i} + d_{2i})$.

Our previous studies of the process of sintering of biocomposites of the BAK-1000 type indicated that the ratio of specific surface areas of the matrix and the filler should be not less that 10.

To estimated the sinterability of mixtures considered, the sinterability index S_t was introduced, which represents the ratio of the specific surface areas of glass and HA powders (S_{gl}/S_{HA}). Experimental results of studying the sinterability of mixtures with different contents of HA are shown in Fig. 1. Three areas of sinterability of mixtures, *A*, *B*, and *C*, are indicated on the dependence of the sinterability index on the content of HA at the temperature of 800°C and under 45-min exposure.

Area *A*: sinterability index is within a range of $30 \geq S_t \geq 12$. Using mixtures with such S_t produces strong and well sintered samples with required porosity and volumetric mass values depending on the fractional composition and content of HA. In area *B* with $S_t < 12$ samples do not sinter in the time-temperature conditions considered. In area *C*, formation of dense vitreous materials with different degrees of porosity is registered. In the interval of $30 < S_t < 61$ the pore size and pore distribution depend on the fractional composition of HA.

Sinterability index being equal, the kind of emerging pores depends on the size of HA particles. It is established that as their size increases, the volume of intergrain voids grows, and this, in turn, results in an increased size of pores in sintered composite. The intergrain hollow space in a sample consisting of densely packed glass and HA particles is a sum of intergrain voids, whose configuration depends on the type of packing of particles. The most probable pore shapes in a descending order may be as follows:

– tetrahedral, is a pore if formed by four spherical particles;

– hexahedral formed by six spheres;

– octahedral pore formed by eight particles.

Assuming all material particles to be spherical and each pore to be formed by particles of equal size, we calculated the volume of intergrain voids taking the pore to be a tetrahedron, whose volume V depends on the size of the particles forming this void:

$$V = \frac{2}{3}Sh,$$

where S is the surface area of the tetrahedron base, m², and h is the height of the tetrahedron, m.

Calculation results indicated that varying the size of HA granules from 600 to 40 μm decreased the size of intergrain voids from 150 to 10 μm. It was similarly determined that the size of intergrain voids in powder consisting of spherical granules is equal to 50% of their radius.

Hence it follows that the content of HA in sintered composite material may be increased to 60% and even more, provided that it is added to the mixture for sintering in the form of granules sized 500 μm and more. However, in this case large pores are formed and the strength of the material decreases perceptibly.

Considering the purpose of the study, i.e., production of strong fine-pore material for dentistry. the working interval of HA fractions was specified in the limits from 40 to 260 μm, and the matrix : filler ratio was selected to get the sinterability index within the interval of $30 \geq S_t \geq 12$.

Thus, to model a tooth root implant from the material developed, it can be taken that at $S_t = 20$ the crown part of the implant corresponds to the material with 7% HA. Dentine can be modeled by material containing 25% HA and cement by material with 40% HA.

Based on the results obtained it was established that the structure quality and properties of bioactive composite materials depend on the ratio of the specific surface areas of the components and their granulometric compositions and can be expressed by means of the sinterability index. Analysis of the functional dependence of the sinterability index on HA content $S_t = f(C_{HA})$ shows that it is nonlinear for HA introduced in the form of fine fractions (Fig. 1). When the granule size grows to $200 - 300$ μm, this dependence tends to be linear. This dependence can be expressed as follows:

$$S_t = R^k,$$

where R is the ratio of a matrix content to a filler content in the material and k is the coefficient characterizing the dispersion and shape of particles of the matrix and filler powders in initial mixtures.

However, this dependence needs to be refined.

In the time-temperature regimes of sintering considered the value interval of $30 \geq S_t \geq 12$ is identified in which sam-
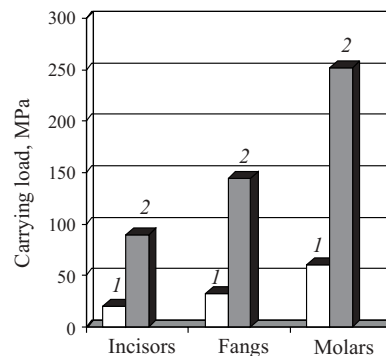

Fig. 2. Compressive load on dental implants: *1*) microporous layer; *2*) dense cortical layer.

ples with required properties can be obtained: volumetric mass from 900 to 1300 kg/m^3, open porosity from 20 to 60% and more. Their compressive strength ranges in the limits from 10 to 50 MPa. This strength of dense microporous and porous materials is sufficient for making laminar dental implants. Figure 2 shows the compressive load carried by implants of average sizes.

Thus, by varying the values of sinterability indexes of components of biomaterials or specifying these values, it is possible in the first approximation to predict the porous structure, mechanical strength, and biological properties of material.

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